— SECTION B —

CHEMICAL SCIENCES

Contents

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THE REACTION OF MALEIC ANHYDRIDE WITH POLYNUCLEAR AROMATIC HYDROCARBONS[1]

By R. Norman Jones, C. J. Gogek, and R. W. Sharpe

Abstract

The first part of this paper is concerned with a quantitative investigation of the reaction of various polynuclear aromatic hydrocarbons with maleic anhydride. In the second part a micromethod for the separation of mixtures of polynuclear aromatic hydrocarbons, based on this reaction, is described. These studies were undertaken in anticipation that such mixtures might occur in carcinogenic extracts from biological sources.

The reaction of maleic anhydride with aromatic hydrocarbons has been reviewed by Norton (14), and has been investigated in some detail by Bachmann and Kloetzel (1) and by Bergmann and Eschinazi (3). In the typical case of anthracene (I) reaction results in the formation of 9, 10-dihydroanthracene-9,10-*endo*-α,β-succinic anhydride (II), which is hydrolyzed by alkali to the 9,10-*endo*-succinate salt (III). Several methods have been described in the literature for the reversal of such diene addition reactions (2, 8, 10) and these should permit of the recovery of the original hydrocarbon from (II) or (III).

These considerations suggested that mixtures of polynuclear aromatic hydrocarbons might be fractionated by the action of maleic anhydride into reacting and non-reacting groups; these could then be separated from one another by taking advantage of the solubility of the *endo*-succinate potassium salts in aqueous alkali. The spectrophotometric analysis of polynuclear aromatic hydrocarbons can be performed on a few micrograms (12), so that such a method would be potentially applicable to very small quantities of material. In the work described here, quantities of the order of 1 to 10 mgm. were employed.

Bachmann and Kloetzel (1) demonstrated that the reaction between anthracene and maleic anhydride obeys the law of mass action. Increase in the concentration of maleic anhydride favors formation of the adduct, while increase in temperature accelerates attainment of equilibrium, but also favors

dissociation. The optimum conditions for reaction established by these investigators were followed, as far as possible, in the experiments described below.
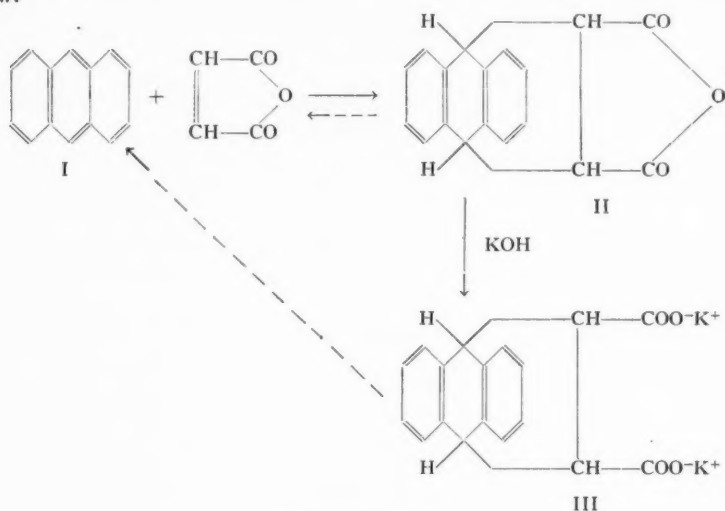
Experimental

A. *The Reactivity of Various Hydrocarbons Towards Maleic Anhydride*

In Table I the hydrocarbons examined are listed, together with the weights of the unreacted material recovered after treatment with maleic anhydride. The reactions were carried out in benzene solution and in molten maleic anhydride without solvent. The effect of the solvent on the reaction was small and not systematic.

In a representative experiment, 5 to 10 mgm. of the hydrocarbon was weighed accurately on a microbalance and transferred to a soft-glass reaction tube (50 mm. long by 5 mm. diameter) which had previously been closed at one end and drawn out ready for sealing at the other. Molten maleic anhydride was added by means of a drop-pipette. The number of drops were counted and the weight of the reagent estimated from the mean weight per drop. Between 100 and 200 moles of maleic anhydride per mole of hydrocarbon was used. In cases where a solvent was employed it was added by pipette after the maleic anhydride had solidified.

The tubes were cooled in ice and sealed, and then heated at 115° to 120° C. for 12 hr. After cooling they were opened and transferred to a 400 ml. beaker containing 50 ml. of water. Ten milliliters of 40% aqueous potassium hydroxide solution was added, the beaker covered with a watch glass, and the solution boiled to hydrolyze the anhydrides. During this reaction any unchanged hydrocarbon rose to the surface. In cases where the unreacted

hydrocarbon was appreciably volatile in steam (e.g., phenanthrene) the hydrolysis was carried out under reflux in the presence of 10 ml. of benzene. After cooling, the solution was extracted with three 10 ml. portions of benzene,

TABLE I

RECOVERY OF HYDROCARBONS AFTER TREATMENT WITH MALEIC ANHYDRIDE

Hydrocarbon (4 to 10 mgm.)	Solvent	Moles of maleic anhydride per mole of hydrocarbon	Unchanged hydrocarbon recovered, %
A. Reactive hydrocarbons			
Anthracene	None	100	0
	Benzene	105	0
1,2-Benzanthracene	None	125	0
	Benzene	125	0
20-Methylcholanthrene	None	115	3.5
	Benzene	115	4.3
1,2,5,6-Dibenzanthracene	None	210	0
	Benzene	195	1
B. Non-reactive hydrocarbons			
Fluorene	None	42	98
Fluoranthrene	None	58	97
Phenanthrene	None	105	100
	Benzene	100	96
Pyrene	None	95	99
	Benzene	95	99
Chrysene	None	75	105
	Benzene	75	100
3,4-Benzpyrene	None	125	86
	Benzene	120	92

the benzene extracts pooled and washed once with water.*   The benzene was removed by evaporation in a stream of nitrogen, and the residue dissolved in boiling ethanol, transferred to a volumetric flask, and, after cooling, the volume was adjusted to 10. ml.   In the case of chrysene it was found necessary to increase this volume to 100 ml. because of the low solubility.

* In these initial experiments the aqueous phase remaining after benzene extraction was discarded.   Later it was worked up for recovery of the endo-succinates as described in Section F.

B. Spectrophotometric Analysis

These ethanolic solutions contained the unreacted hydrocarbon, and the concentrations were determined by ultraviolet spectrophotometry using a Beckman model DU spectrophotometer.

The intensities of absorption at selected maxima are readily expressed in terms of the extinction coefficient $E_{1cm.}^{1\%}$ defined by Equation (1).

$$E_{1cm.}^{1\%} = \frac{1}{c.l} \cdot \log_{10} \frac{I_0}{I} \qquad (1)$$

where c = concentration of solute in grams per 100 ml. of solution,

l = cell length, in centimeters,

$\log_{10} \frac{I_0}{I}$ = optical density at the selected wave length.

The values of $E_{1cm.}^{1\%}$ at the wave lengths used in these measurements are listed in Table II.

TABLE II

SPECTROGRAPHIC CONSTANTS USED IN ANALYSIS OF HYDROCARBONS

Hydrocarbon	Maxima, Å	$E_{1cm.}^{1\%}$ (ethanol solution)
Fluorene	2610	1165
	2890	352
	3000	547
Fluoranthrene	2760	1170
	2870	2090
	3230	322
	3420	416
	3580	428
Anthracene	3240	160
	3395	294
	3565	435
	3755	412
Phenanthrene	2740	709
	3230	17.2
	3300	15.5
	3380	12.6
	3460	13.7
1,2-Benzanthracene	3270	294
	3410	344
	3580	225
20-Methylcholanthrene	3270	159
	3430	230
	3590	283
Pyrene	3185	1440
	3345	2400
	3510	31.2
	3570	19.7
	3620	15.6

TABLE II—*Concluded*

SPECTROGRAPHIC CONSTANTS USED IN ANALYSIS OF HYDROCARBONS—*Concluded*

Hydrocarbon	Maxima, Å	$E_{1 cm.}^{1\%}$ (ethanol solution)
Chrysene	3440	30.4
	3530	15.9
	3610	28.6
3,4-Benzpyrene	3465	523
	3640	954
	3840	1151
1,2,5,6-Dibenzanthracene	3330	627
	3480	558
	3725	37.8
	3825	15.7
	3930	40.5

The ethanolic solution obtained by the procedure outlined above was accurately diluted (10 to 100-fold) so as to give an optical density of between 0.1 and 0.5 in a 1 cm. cell. The optical density was then measured at the wave lengths of two or more selected absorption maxima. A few measurements were taken also on each side of the maxima to establish the sharpness of the peaks as a check on gross contamination. The concentrations were then calculated from Equation (1). For each separate analysis the mean concentration based on averaged values for two or more peaks was accepted; the values listed in Table I are the averaged values for two separate analyses of each hydrocarbon.

Control experiments were performed in which maleic anhydride, alone or with benzene, was carried through the reaction procedure to determine the significance of extraneous absorption. These yielded solutions which were optically transparent at the dilutions employed over the range of spectrographic measurement (2600 to 3950 Å).

C. *Reversal of the Diene Addition Reaction*

The recovery of reactive hydrocarbons from the *endo*-succinate derivatives has not been examined extensively by earlier investigators, although the reverse diene synthesis has been employed in other connections. Bachmann and Kloetzel (2) used it in the preparation of 3,4-cyclopentenophenanthrene and related compounds. They dry distilled the calcium salts of the hydrolyzed adducts with calcium oxide, sometimes with the addition of zinc dust. They also refluxed the quinoline salts of the hydrolyzed adducts with basic copper carbonate. The reverse diene synthesis has been used also by Fieser,

Fieser, and Hershberg (10) in the synthesis of polynuclear aromatic hydro-carbons. A direct decomposition of the anthracene adduct has been reported by Dermer and King (8) who pyrolyzed 9,10-dihydroanthracene-9,10-*endo-*α,β-succinic anhydride with an excess of soda lime, and obtained an 80% recovery of anthracene by sublimation. The experiment of Dermer and King has been repeated in our laboratory and extended to determine the optimum conditions for anthracene recovery. Adducts of other reactive hydrocarbons have also been prepared and the reversal of the diene addition reaction examined.

D. Preparation of Crystalline Adducts

(a) *Anthracene.*—The hydrocarbon (15 gm.) and maleic anhydride (27 gm.) were added to 300 ml. of benzene and the solution refluxed for 90 min. On cooling, 9,10-dihydroanthracene-9,10-*endo-*α,β-succinic anhydride separated from solution and was recrystallized from aqueous acetone. Yield 15 gm. (64%).

(b) *1,2-Benzanthracene.*—The hydrocarbon (2 gm.) was added to maleic anhydride (1 gm.) dissolved in 40 ml. of xylene, and refluxed overnight. On cooling, crystals of the *endo-*succinic anhydride separated and were recrystal-lized from xylene to yield 0.9 gm. (m.p. 240° to 241° C.). Yield 63%.

(c) *1,2,5,6-Dibenzanthracene.*—The hydrocarbon (1 gm.) was added to 17.7 gm. of maleic anhydride dissolved in 30 ml. of xylene and refluxed for one hour. On cooling, the *endo-*succinic anhydride separated and was recrystal-lized from aqueous acetone. Yield, 1 gm. (74%).

E. Decomposition of the Endo-succinic Anhydrides

About 4 mgm. of the adduct was weighed on a microbalance and transferred to a microsublimation tube similar to that described by Riegel (16). Finely powdered soda lime (7 to 10 mgm.) was added, the cold-finger inserted, and the tube placed in a bath of molten potassium nitrate – sodium nitrite at 400° to 430° C. Sublimation of the hydrocarbon occurred rapidly and after 30 min. the cold-finger was withdrawn and the adhering hydrocarbon washed into a 100 ml. volumetric flask with hot ethanol. When cool, the volume was adjusted and the hydrocarbon analyzed spectrophotometrically as described in Section *B*. In the first experiments the sublimations were carried out *in vacuo*, but it was later found that the reaction proceeded equally satis-factorily at atmospheric pressure.

The recoveries obtained are summarized in Table III. In the case of anthracene, a series of determinations were carried out over a range of decom-position temperatures. These indicated that the recovery improved as the temperature was raised, and in subsequent experiments the maximum attain-able temperature was used.

TABLE III

RECOVERY OF HYDROCARBONS FROM CRYSTALLINE ADDUCTS

Hydrocarbon	Wt. of adduct, mgm.	Wt. of soda lime, mgm.	Temp., °C.	Time of heating, hr.	Recovered hydrocarbon	
					Wt., mgm.	%
Anthracene	8.05	15	235	3	1.14	22
"	6.21	11	280	1	2.34	58
"	3.17	7.5	325	1	1.46	72
"	4.37	7.5	400	0.5	2.40	86
"	3.86	9.5	405	0.5	2.32	94
"	4.27	7.5	430	0.5	2.52	91
1,2-Benzanthracene	2.00	6.0	430	0.5	1.09	78
"	2.32	6.0	430	0.5	1.38	85
"	1.51	5.0	430	0.5	0.82	77
1,2,5,6-Dibenzanthracene	1.76	4.0	480	0.5	1.09	86
"	2.29	6.0	480	0.5	1.45	86

F. Separation of Mixtures of Reactive and Non-reactive Hydrocarbons

The recoveries of reactive hydrocarbons under the optimum conditions lay between 75 and 95%. These, although not quantitative, seemed sufficiently high to justify the extension of these studies to the separation of hydrocarbon mixtures.

In the experimental procedure outlined in Section *A* the unreacted hydrocarbons were separated from the reaction products by benzene extraction, leaving an aqueous solution. To recover the reacted hydrocarbons, this aqueous solution was acidified with a few drops of concentrated hydrochloric acid and extracted with three 10 ml. portions of ether. The bulked ether extracts were washed with water and the solvent removed on a water bath in a stream of nitrogen. The residue was powdered and an excess of finely powdered soda lime added. The mixture was dry distilled as described in Section *E* and the recovered hydrocarbons analyzed spectrophotometrically.

The results of a series of experiments on three pairs of binary mixtures of reactive and non-reactive hydrocarbons are given in Table IV. In these cases the recoveries from the reactive hydrocarbons were somewhat lower than those obtained in the decomposition of the crystalline anhydrides (57 to 78%). Part of the loss might result from the extra manipulation involved and from side reactions occurring during the treatment of the hydrocarbon with maleic anhydride. It should also be observed that whereas the dry distillations reported in Section *E* involved reaction of soda lime with the anhydrides, in these experiments the product obtained by acid extraction of the potassium salt was used. Presumably this was the free dicarboxylic acid, so that the conditions obtaining during the dry distillations were not strictly comparable.

TABLE IV

SEPARATION OF MIXTURES OF REACTIVE AND NON-REACTIVE HYDROCARBONS

Hydrocarbons	Wt., mgm.	Recovery, %
A. *Anthracene and phenanthrene*		
Anthracene	5.26	81
Phenanthrene	5.33	74
Anthracene	5.22	79
Phenanthrene	5.21	78
B. *1,2-Benzanthracene and pyrene*		
1,2-Benzanthracene	4.94	57
Pyrene	4.70	100
1,2-Benzanthracene	5.51	62
Pyrene	5.35	102
C. *1,2,5,6-Dibenzanthracene and 3,4-benzpyrene*		
1,2,5,6-Dibenzanthracene	4.73	71
3,4-Benzpyrene	5.30	92
1,2,5,6-Dibenzanthracene	4.89	67
3,4-Benzpyrene	5.75	94

Discussion

From the experimental results listed in Table I it is seen that the hydro-carbons fall quite sharply into reacting and non-reacting groups, and no case was observed in which a partial reaction took place. The reactivity of anthracene (1, 5), of 1,2-benzanthracene (5), and 1,2,5,6-dibenzanthracene (6) has been reported previously. The non-reactivity of phenanthrene, fluorene, and chrysene is in accord with the absence of marked diene reactivity in these compounds and with their high aromatic stability. In 3,4-benzpyrene the presence of a linear tricyclic system suggests by analogy with anthracene that maleic anhydride might add as in IV, but earlier investigators (7) have also failed to demonstrate this reaction. The yields of hydrocarbons recovered on thermal decomposition of the adducts are substantially higher than those reported previously in the scattered observations of other workers.

IV
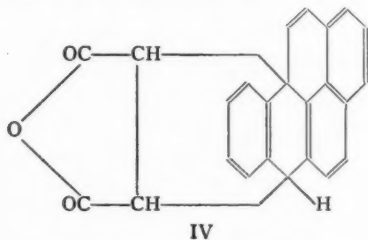
Interest in the fractionation of micro-quantities of mixtures of such com-pounds arose initially from the fact that certain of these hydrocarbons are carcinogenic and the establishment of their presence in, or absence from, material of biological origin is of importance (11, 13, 15).

Simple binary mixtures of polynuclear aromatic hydrocarbons can be separated conveniently by adsorption chromatography (4). However, experience in the separation of complex mixtures of other kinds of compounds has shown that some type of chemical fractionation is advisable before resorting to physical methods. Thus, in the fractionation of the complex mixtures of steroid hormone metabolites which occur in urine, it is necessary to carry the materials through two stages of chemical fractionation (using the Girard reagent and digitonin) before complete chromatographic separations can be achieved (9). Complex mixtures of polynuclear aromatic hydrocarbons could be separated by treatment with maleic anhydride in a similar manner and the reacting and non-reacting fractions then submitted to further fractionation by adsorption chromatography or other physical methods.

Acknowledgment

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THE PYROLYSIS OF CAROTENE[1]

By R. Norman Jones and R. W. Sharpe

Abstract

Kuhn and Winterstein reported the isolation of 2,6-dimethylnaphthalene from the products of pyrolysis of carotenoid pigments. The production of alkyl derivatives of phenanthrene and chrysene by the same type of cyclization can readily be formulated. The production of such hydrocarbons by the action of heat on naturally occurring substances, which include common constituents of foodstuffs would be of significance since such compounds might exhibit carcinogenic activity. Fractionation of the products of carotene pyrolysis confirmed the formation of 2,6-dimethylnaphthalene, but no more complex polynuclear aromatic hydrocarbons were isolated. The methods of analysis employed should have permitted the detection of such compounds in amounts considerably below 1%.

Introduction

The carcinogenic activity exhibited by certain pure chemical compounds has led several investigators to search for similar substances in foodstuffs, tobacco smoke, and body tissues (4, 9, 12) in an attempt to demonstrate that such substances might be responsible for the development of "spontaneous" cancer. Among the known types of carcinogenic compounds, the polynuclear aromatic hydrocarbons have received most consideration since the available evidence indicates that endogenous carcinogens, if such indeed exist, accumulate in nonsaponifiable lipid extracts. The structural similarity of desoxycholic acid to 20-methylcholanthrene and its conversion to the latter compound in the laboratory (1, 13) initiated considerable discussion as to the possible role of steroids as precursors of carcinogens. However, the possibility that the naturally occurring carotenoid pigments might act as carcinogen precursors does not appear to have received previous consideration, although simple aromatic hydrocarbons have been produced by the thermal decomposition of such substances.

In 1911 van Hasselt (3) isolated m-xylene as a product of the pyrolysis of bixin, and later Kuhn and Winterstein (7, 8) obtained toluene, m-xylene, and 2,6-dimethylnaphthalene (II) on vacuum distillation of several carotenoids. The reaction was postulated to involve the cyclization of the center chain only, and this was confirmed by the subsequent isolation of 2,6-dimethylnaphthalene on pyrolysis of crocetin dimethyl ester (I), a linear carotenoid.

It is possible to visualize how more complex polynuclear aromatic hydrocarbons might arise by such ring closures for instance β-carotene (III) might yield both 3,6,9-trimethylphenanthrene (IV) and 2,5,8,11-tetramethylchrysene (V). Chrysene and certain of its methyl derivatives have been shown to exert weak carcinogenic activity (2, pp. 85-87).

Kuhn and Winterstein examined only the more volatile fractions of their carotenoid pyrolysis fractions, and it was therefore considered that a more complete study of the products of heat decomposition of the carotenoids

I $R_1 = COOCH_3$

II

III

IV

V

$R_2 =$
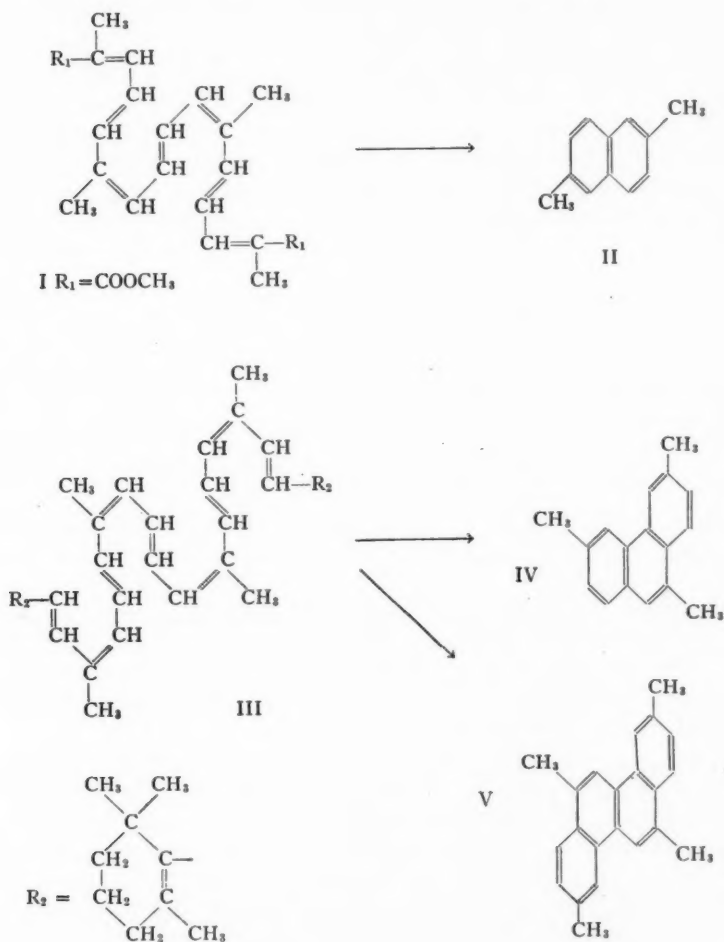
would be worth undertaking.   Methods for the fractionation and identification of polynuclear aromatic hydrocarbons had been developed previously in our laboratories (5, 6) and were readily applicable to carotenoid pyrolyzates.

In these experiments we failed to detect the presence of any polynuclear aromatic hydrocarbons although the formation of 2,6-dimethylnaphthalene was confirmed.

Experimental

A. Fractionation of Pyrolyzed Carotene

One gram of a mixture of 90% β- 10% α-carotene was introduced into a thick-walled glass combustion tube 20 cm. long by 2 cm. diameter, which was repeatedly evacuated, filled with nitrogen, and finally sealed.   The tube was heated in an electric furnace in the dark at 260 $\pm$ 5° C. for 24 hr.   After cooling it contained a viscous highly fluorescent oil which was completely soluble in cold hexane.

This material was submitted to a preliminary chromatographic analysis on a column of Fisher activated alumina 60 cm. long by 1.6 cm. diameter. Details of the fractionation are given in Table I.   The eluates were collected

TABLE I

CHROMATOGRAPHIC ANALYSIS OF PYROLYZED CAROTENE

Group	Eluting agent	Number of 50 ml. fractions	Weight, mgm.	Remarks
I	Hexane	16	334	Pale fluorescent oils
II	Benzene	11	489	"
III	Ether	6	7	"
IV	Acetone	8	55	Dark brown fluorescent oils
V	Ethanol	5	10	"

in 50 ml. fractions.   The fractions in Groups I and II possessed brilliant blue-green fluorescene, while the later fractions were dark and fluoresced only slightly.   The ultraviolet absorption spectra of each of the fractions was determined but none of them exhibited any structure such as would indicate the presence of a polynuclear aromatic hydrocarbon.

Since the Group II fractions fluoresced most brilliantly, they were first selected for further fractionation.   Fraction 2, which accounted for 80% of the weight of Group II, was next submitted to molecular distillation.   During the preparation of the sample, before reduction of pressure, fluffy white crystals began to sublime out of the melt at 75° to 80° C.   The crystals melted at 110° to 111° C. and showed no depression on admixture with a sample of 2,6-dimethylnaphthalene.   The structure was confirmed by the identity of the ultraviolet absorption spectrum with that of 2,6-dimethylnaphthalene.

B. Variation in Yield of 2,6-Dimethylnaphthalene with Pyrolysis Temperature

Attempts were next made to determine the pyrolysis conditions which would give the maximum yield of 2,6-dimethylnaphthalene, in anticipation that such conditions might also be most favorable for the production of other polycyclic hydrocarbons.

About 300 mgm. of the mixture of α- and β-carotene were pyrolyzed as described in the previous section, the furnace being held at a pre-selected temperature. The resulting oil was dissolved in ether, transferred to a molecular still, and the 2,6-dimethylnaphthalene sublimed out at 80° C. and 10^{-4} mm. pressure. The product was dissolved in ethanol and analyzed by ultraviolet spectrometry according to the method described in an earlier publication (6). Measurements were made on the absorption maxima at 3240, 3160, and 3090 Å, the values of $E_{1cm.}^{1\%}$ being 74.5, 38.2, and 55.1 respectively in ethanol solution.

The quantities of 2,6-dimethylnaphthalene obtained at various temperatures are given in Table II. A maximum yield of 1.4% occurred for pyrolysis at 200° C. Kuhn and Winterstein (7) obtained 2.5 mgm. from the pyrolysis of 5 gm. of carotene at 190° C. (0.05%).

TABLE II

YIELDS OF 2,6-DIMETHYLNAPHTHALENE

Wt. of carotene, mgm.	Pyrolysis temperature, ° C.	Yield of 2,6-dimethylnaphthalene	
		Mgm.	%
200	150	0.4	0.20
306	200	4.25	1.4
156	250	1.38	0.9
130	300	Nil	Nil

The less volatile distillates obtained from these reaction products were all oils, and none showed any ultraviolet absorption bands suggestive of the presence of other aromatic hydrocarbons.

C. Recovery of Polynuclear Aromatic Hydrocarbons Added to Carotene Pyrolyzates

To check the sensitivity of the isolation procedures some experiments were performed in which chrysene and 1,2-benzanthracene were added to pyrolyzed carotene.

In the first experiment 20.6 mgm. of chrysene was added to 206 mgm. of pyrolyzed carotene from which the 2,6-dimethylnaphthalene had been removed by sublimation. The mixture was dissolved in benzene to assure a uniform distribution and transferred to a molecular still. The product was distilled at 5×10^{-3} mm. and the temperature raised at a rate of about 1° per minute to 120° C. and then more slowly. An oily crystalline product distilled out between 120° and 140° C. This was dissolved in 3 ml. of benzene and chromatographed on activated alumina. The chromatogram was developed with 95% hexane – 5% benzene mixture. Two separate blue fluorescent zones formed, one of which remained at the top of the column while the second moved rapidly down. The lower zone was sectioned out and eluted

with ethanol.   On removal of the solvent, crystalline material separated and
was identified as chrysene by the ultraviolet absorption spectrum.   The
amount recovered, determined spectrophotometrically was 11 mgm. or 56%
of the amount added.

In a second experiment 1.77 mgm. of 1,2-benzanthracene was added to
82.4 mgm. of pyrolyzed carotene and 0.65 mgm. (38%) recovered in a similar
manner.

The latter experiment indicated that quantities of polynuclear hydro-
carbons of the order of 1 to 2% of the total weight of the pyrolyzate should
have been isolated.   The minimum quantity detectable spectrographically
would have been much below this, probably not greater than 0.1% of the
total weight.

D.   Molecular Weight of Pyrolyzate Fractions

The major part of the pyrolyzates, which exhibited intense blue fluorescence
and ready solubility in hexane, was presumably a mixture of polymerization
products.   The degree of polymerization in a selected series of fractions was
investigated by determination of the mean molecular weight using the micro-
Rast technique (10, 11).

Carotene was pyrolyzed at 200° C. for 24 hr. and the 2,6-dimethylnaphtha-
lene removed by sublimation.   The residue was fractionated in a molecular
still at 10^{-4} mm., the fractions distilling at 150°, 200°, and 250° C. being
collected separately.   The molecular weight of each fraction and of the
residue in the still-pot was determined at each stage.   The results, as shown
in Table III, indicate a mean molecular weight of 900 to 1000 for the earlier
distillates, increasing in a regular manner with diminishing volatility.

TABLE III

MEAN MOLECULAR WEIGHTS OF PYROLYZED CAROTENE FRACTIONS

Temperature, ° C.	Fraction	Mol. wt.
150	Residue	905
200	Distillate	1060
	Residue	1650
250	Distillate	1220
	Residue	1860
300	Residue	8015

Conclusions

These experiments confirmed the findings of Kuhn and Winterstein con-
cerning the formation of 2,6-dimethylnaphthalene.   They indicated also that
if any tricyclic or tetracyclic polynuclear hydrocarbons are formed at the
same time, they must be present in concentrations of 0.1% or less.

The conditions existing in the molten carotenoid favor intermolecular rather than intramolecular condensation, and the formation of 2,6-dimethyl-naphthalene from the central part of the chain must be attributed to special conditions, possibly a favored folding of the chain in one of the thermolabile *cis*-configurations (14). The possibility of 2,6-dimethylnaphthalene arising from the subsequent thermal decomposition of the polymer might be considered, but if this were so one would expect it to be formed continuously during the course of molecular distillation.

If the rate of intermolecular condensation could be diminished, conditions more favorable to the production of tri- and tetra-cyclic rings systems would be established. This might be brought about by heating carotene in dilute solution in a high boiling paraffin or a triglyceride. Further experiments along these lines are contemplated.

Acknowledgment

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DETERMINATION OF THE MAXIMUM ENERGY OF
THE β^- RADIATION OF S[35] [1]

By L. Yaffe and Katharine M. Justus

Abstract

The range in aluminum of the β^- radiation of S[35] has been determined and found to be 32.2 ± 0.3 mgm. per cm². Using various range–energy relations the maximum energy has been estimated to be 169 ± 5 kev.

Introduction

In the course of investigations on the back-scattering of electrons (12) it became necessary to determine accurately the maximum energy of the β^- particles emitted by S[35].

Kamen (6) obtained a value of 120 ± 15 kev. with absorption methods using aluminum and cellophane. Libby and Lee (8) using a screen wall counter and a magnetic deflection method obtained the value 107 ± 20 kev. Overman (9) using a windowless counter and absorption methods reported a range of 35 mgm. per cm² and a corresponding energy of 170 kev. Solomon, Gould, and Anfinsen (11) by absorption in aluminum give a range value of 31.4 ± 0.6 mgm. per cm² and a corresponding energy of 167 ± 4 kev. The last mentioned authors also report a private communication from R. K. Osborne which gives a beta-ray spectrometer value of 169 ± 3 kev.

The work on back-scattering showed that the maximum energy of S[35] must be greater than that of C[14] (154 kev.), and to verify this an attempt was made to get as accurate a determination as possible.

Experimental

The S[35] used was of very high specific activity. The samples were counted using a bell-jar type counter with a 1.9 mgm. per cm² mica window and the sample was 1 cm. from the counter window. A sample of S[35] (about 10,000 counts per min. in our geometry) was then pipetted on to a thin Formvar film (50 μgm. per cm².) and evaporated to dryness. Various absorbers were placed in position and the count recorded until the original was reduced by a factor 10. An additional sample was then added to the original one so that the count was about 10,000 per min. with the last absorber used in position and additional absorbers were then added. This procedure was repeated until no more decrease in counts was noted, never counting less than 1000 counts per min. In this manner, the end point could be determined quite accurately. The final sample used had an activity of 585,000 counts per min. in our geometry (5.85 × 10⁶ disintegrations per min.). The final sample had a mass less than 1 μgm. per cm² and approximated a point source.

Results

The absorption curve for S^{35} in aluminum is shown in Fig. 1.   The samples were all related to the original one by ratios to give a continuous curve with very high accuracy even at the lower end of the curve.   A residual back-
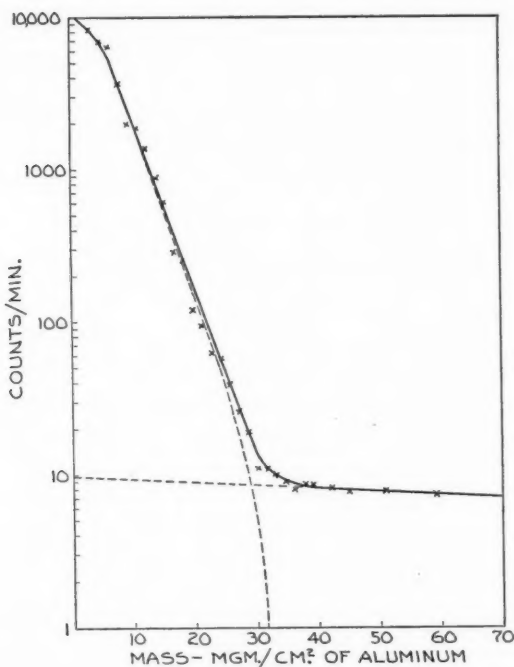

FIG. 1. S^{35} *absorption curve.*

ground of 0.1%, probably due to P^{32} introduced by the reaction Cl^{35} (n, α) P^{32} in the originally irradiated potassium chloride, is present and this was subtracted to give the S^{35} curve.

A visual examination, which gave good accuracy owing to the method used in obtaining the absorption curve, gave a range of 31.9 mgm. per cm. (corrections having been made for the air gap between counter window and sample and counter window thickness).   The Feather (2) method was employed using UX_2 and this gave a range of 32.6 mgm. per cm.   Attempts to use RaE and Co^{60} with this method were not successful owing to the differences in the shapes of the absorption curves.   The range was thus determined to be 32.2 ± 0.3 mgm. per cm.²

Energies were determined using the following relations, where R is the range and E the energy:

(i) Glendenin curve (4), 170 ± 5 kev.

(ii) Libby (7) relation, $E = (150 \times R)^{\frac{1}{2}}$, where E is in kev. and R in mgm. per cm.^{2} aluminum

$$E = 162.5 \pm 1.5 \text{ kev.}$$

(iii) Flammersfeld (3), $E = 1.92 \, (R^2 + 0.22R)^{\frac{1}{2}}$, where E is in Mev. and R in gm. per cm.^{2} aluminum

$$E = 173 \pm 1 \text{ kev.}$$

If these methods are weighted equally, the energy is 169 ± 5 kev. The value found by the back-scattering method was 165 ± 5 kev.

For β emitters up to energy values of 200 kev., Libby (7) gives the following relations:

$$\alpha R = k_1 , \qquad\qquad (1)$$

where α is the mass absorption coefficient, R is the range and k_1 is a dimensionless constant; and

$$\frac{R}{d_{\frac{1}{2}}} = k_2 , \qquad\qquad (2)$$

where $d_{\frac{1}{2}}$ is the external absorption half-thickness value in the same units as R.

Using the value of $\alpha = 0.32$ obtained by Henriques *et al.* (5), Libby puts $k_1 = 5$. A similar relation has previously been proposed by Chalmers (1) who obtained a value for $k_1 = 7.5$, using more energetic β^- rays. This relation was reviewed by Sargent (10) for UX_2 and RaE with values of 6.5 and 8.5 respectively obtained for k_1. Our value of $\alpha = 0.266$ cm.^{2} per mgm. aluminum with $R = 32.2$ mgm. per cm.^{2} aluminum gives $k_1 = 8.6$. This is in good agreement with the work of Solomon *et al.* (11) for the value of k_1 and with a private communication of Henriques to Solomon (11) for the value of α for S^{35}.

Since $k_1 = 0.693 \, k_2$, Libby gets the value of 7.2 for k_2. Owing to the shape of the absorption curve it is difficult to assign a single value for $d_{\frac{1}{2}}$ over its entire range. Over the linear portion of the curve $d_{\frac{1}{2}} = 2.6$ mgm. per cm.^{2}, yielding a value of $k_2 = 12.4$.

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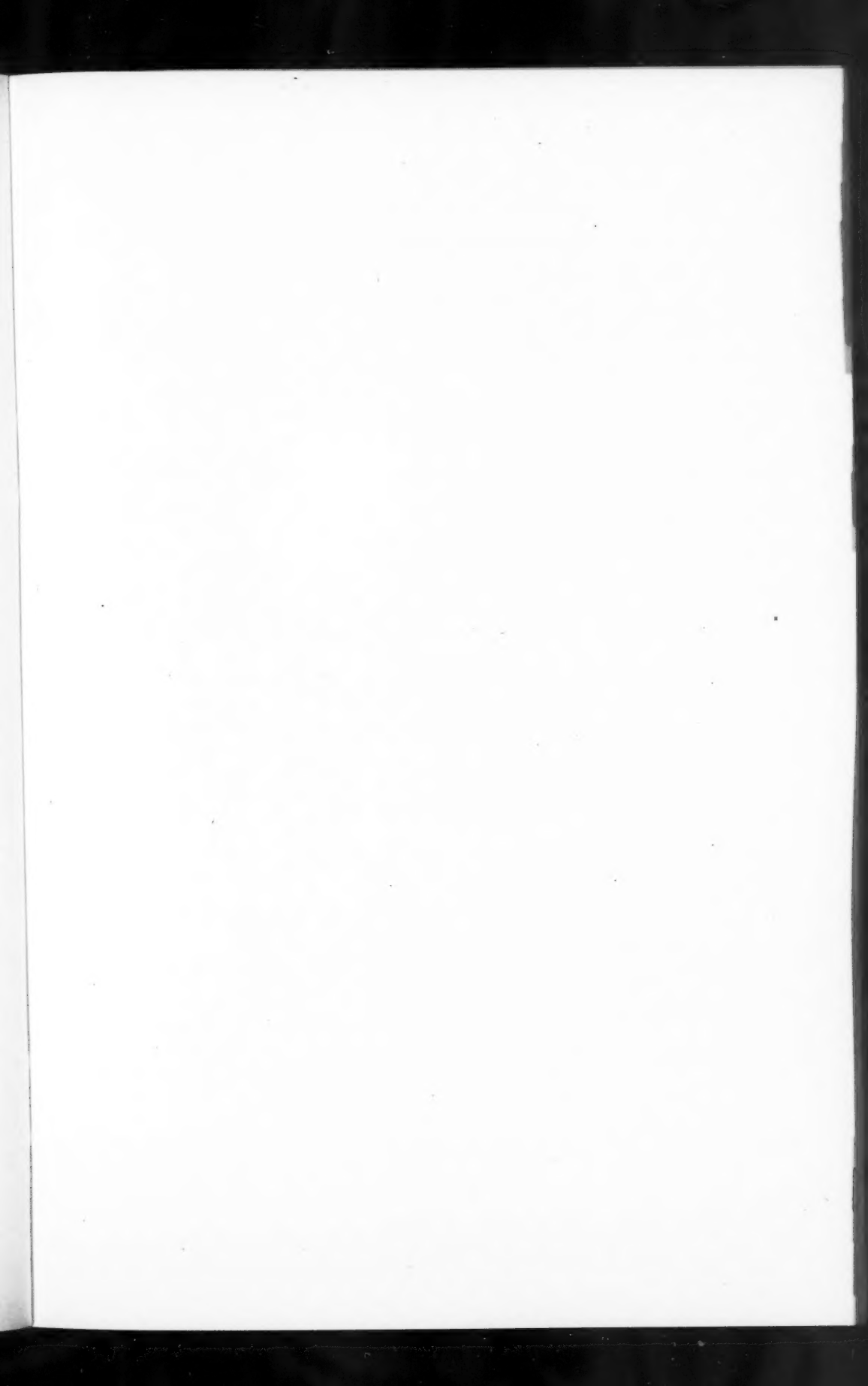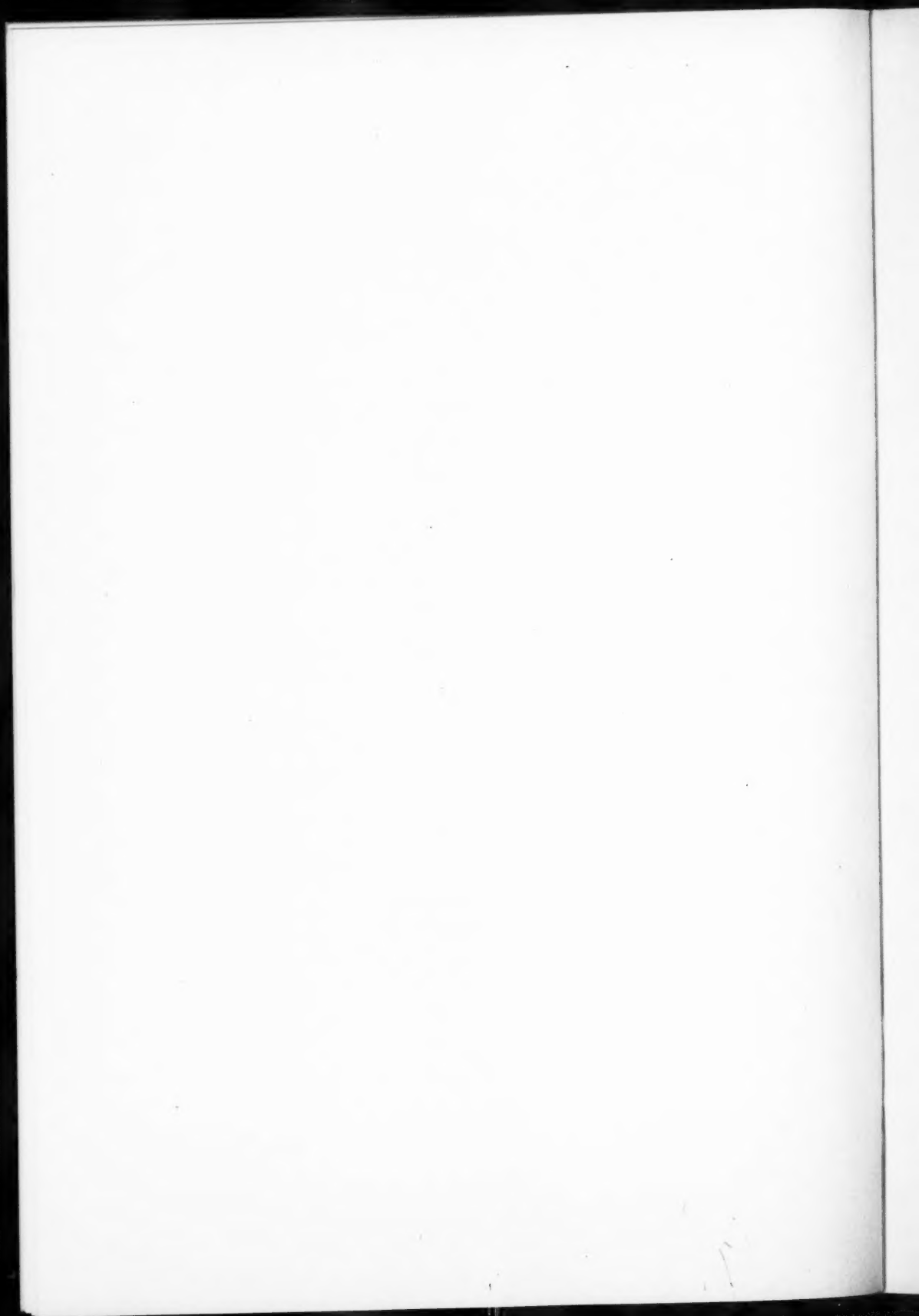
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